



Large-scale fabrication of superhydrophobic polyurethane/nano- Al_2O_3 coatings by suspension flame spraying for anti-corrosion applications



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ABSTRACT

This study aims to further enhance the anti-corrosion performances of Al coatings by constructing superhydrophobic surfaces. The Al coatings were initially arc-sprayed onto steel substrates, followed by deposition of polyurethane (PU)/nano- Al_2O_3 composites by a suspension flame spraying process. Large-scale corrosion-resistant superhydrophobic PU/nano- Al_2O_3 -Al coatings were successfully fabricated. The coatings showed tunable superhydrophilicity/superhydrophobicity as achieved by changing the concentration of PU in the starting suspension. The layer containing 2.0 wt.%PU displayed excellent hydrophobicity with the contact angle of $\sim 151^\circ$ and the sliding angle of $\sim 6.5^\circ$ for water droplets. The constructed superhydrophobic coatings showed markedly improved anti-corrosion performances as assessed by electrochemical corrosion testing carried out in 3.5 wt.% NaCl solution. The PU/nano- Al_2O_3 -Al coatings with superhydrophobicity and competitive anti-corrosion performances could be potentially used as protective layers for marine infrastructures. This study presents a promising approach for fabricating superhydrophobic coatings for corrosion-resistant applications.

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1. Introduction

Various strategies in particular coating technologies have been developed to protect steel structures from corrosion [1–3]. Aluminum coatings proved to be one of the most economical corrosion protection systems for the marine environment [4]. However, long-term use of aluminum coatings is limited since they usually contain intrinsic flaws, such as numerous pores [5,6]. In recent years, superhydrophobic coatings as corrosion inhibitors have attracted considerable attentions [7–11]. In theory, superhydrophobic surfaces resist intimate contact of surrounding corrosive media, in turn enhancing corrosion resistance of the matrix structure [12]. Therefore, construction of superhydrophobic surfaces for the corrosion-resistant Al coatings might be a promising approach for enhanced properties for marine applications.

Generally, superhydrophobic surfaces are water repellent with large water static contact angle ($\text{CA} > 150^\circ$) and small sliding angle ($\text{SA} < 10^\circ$). The superhydrophobicity provides the surfaces with versatile potential for a variety of applications such as self-cleaning

[13,14], anti-biofouling [15], anti-icing [16,17], drag-reducing [18,19], and corrosion resistance [20,21]. The wettability of solid substances is known to be dependent on their surface chemical composition [22] or topographic structure [23]. Many approaches have been attempted to fabricate superhydrophobic surfaces, for example sol-gel processing [24], lithography [25], electrodeposition [26], layer-by-layer deposition [27], electrospinning [28], and chemical vapor deposition [29], etc. Yet, application of most of the above techniques for large-scale fabrication of superhydrophobic surfaces is questionable. Searching cost-effective fabrication techniques has therefore been one of the current research goals for construction of hydrophobic surfaces with desirable properties.

Suspension thermal spray is an exciting method suitable for fabricating nanostructured coatings due to its unique advantages of circumventing the preparation of micron-sized powder feedstock and retaining the chemistry of the nanostructured materials [30]. Recently, we have successfully fabricated hybrid micro-/nanostructured titania coatings by flame spraying liquid feedstock [31]. The approach was also employed to deposit TiO_2 and SiO_2 nanoparticles on paperboard surfaces for mediated wetting properties [32]. The difficulties for depositing the coatings with tailorable wettability are how to control simultaneously the chemical and physical properties of their surfaces. There are so far very few

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studies on suspension flame sprayed superhydrophobic coatings. In this paper, corrosion-resistant Al coatings were deposited on stainless steel substrate, followed by further suspension flame spray construction of superhydrophobic layer on the Al coatings. Polyurethane (PU)/nano- Al_2O_3 suspension was employed for the deposition of the superhydrophobic layer, wettability of which was tunable as accomplished by altering the concentration of PU in the starting suspension. Comprehensive microstructural characterization and corrosion-resistance assessment gave clear insight into potential applications of the superhydrophobic layers for marine applications.

2. Experimental setup

Stainless steel (316L) plates with dimensions of $20\text{ mm} \times 30\text{ mm} \times 1.5\text{ mm}$ and $300\text{ mm} \times 300\text{ mm} \times 1.5\text{ mm}$ were used as the substrates. The high velocity arc spray (HVAS) system (TLAS-500C, China) was employed to deposit the aluminum ($\varnothing 2\text{ mm}$ Al wire, Beijing General Research Institute of Mining & Metallurgy, China) coatings on the substrates. Prior to the spraying, the substrates were surface grit blasted using 60 mesh black fused alumina sand and subsequently degreased by sonication cleaning in acetone. For the arc spraying, the current and voltage of the arc were 100A and 25V respectively, and the spray distance was 150mm. The compressed air with the pressure of 0.5MPa was used as auxiliary gas. Further PU/ Al_2O_3 coating deposition was made on the as-sprayed Al coatings. The PU/nano- Al_2O_3 suspension was sprayed via a suspension flame spraying method according to an established protocol [31]. For the PU/nano- Al_2O_3 suspension preparation, Al_2O_3 nanoparticles of $\sim 100\text{ nm}$ (Aladdin Chemistry Co. Ltd., China) were added into distilled water with a concentration of 3.0 wt.% and the suspension with PU concentration of 0 wt.%, 0.1 wt.%, 0.5 wt.%, 2.0 wt.% and 3.0 wt.% was investigated. For comparison purpose, both the Al_2O_3 and the PU/ Al_2O_3 suspensions were sprayed for coating deposition. The flame spray system (Wuhan Research Institute of Materials Protection, China) was employed for the suspension spraying. The suspension feed rate was 30 ml/min and spray distance was 150 mm.

Microstructure of the powder and the coatings was characterized by transmission electron microscopy (TEM, JEOL2100, Japan) and field emission scanning electron microscopy (FESEM, FEI Quanta FEG250, the Netherlands). Chemical composition of the samples were detected by X-ray diffraction (XRD, Bruker AXS, Germany) at a scanning rate of $0.1^\circ/\text{s}$ using $\text{Cu K}\alpha$ radiation operated at 40 kV. Contact angle measurement was performed using a video-based optical system (Dataphysics OCA20, Germany) operated at ambient temperature. Three samples were measured for each type of the coatings and five points were tested for each sample. Chemistry of the samples was further characterized by Fourier transform infrared spectroscopy (FTIR, model 6300, Bio-Rad Co. Ltd., USA). The powder and the crushed coating samples were mixed with dried potassium bromide (KBr) powder at a concentration of $\sim 0.2\text{ wt.}\%$ and subsequently compressed to produce transparent tablet. The infrared spectrum with a resolution of 8 cm^{-1} and the scan number of 4 was adopted with a spectral region from 400 to 4000 cm^{-1} . The corrosion resistance of the samples was investigated by potentiodynamic polarization testing in 3.5 wt.% NaCl solution operated at room temperature using a PGSTAT302 electrochemical workstation equipped with a three-electrode cell system. Platinum electrode was used as the counter electrode, and the samples were working electrode, and a saturated calomel electrode acted as the reference electrode. Polarization curves were acquired at a scanning rate of 0.01 V/s from -2.0 to 0.5 V .

3. Results and discussion

To prepare the PU/ Al_2O_3 suspension, the Al_2O_3 nanoparticles were dispersed in PU aqueous solution. The untreated starting Al_2O_3 nanoparticles were analyzed by XRD. As shown in Fig. 1a, the diffraction peaks referring to single phase $\alpha\text{-Al}_2\text{O}_3$ have been found for the untreated starting Al_2O_3 nanoparticles (JCPDS Card No.: 42-1468) [33]. No impurities were detected in the starting powder. The morphologies of untreated and PU treated Al_2O_3 nanoparticles are shown in Fig. 1b and c, respectively. The untreated Al_2O_3 nanoparticles were relatively well-dispersed with the size of $\sim 100\text{ nm}$ in diameter (Fig. 1b). Clear aggregation is seen for the Al_2O_3 nanoparticles after the surface treatment with PU (Fig. 1c-1). Further TEM characterization confirms the unique dispersion of Al_2O_3 nanoparticles in PU (Fig. 1c-2).

The XRD and FTIR analyses suggest well-retained structure of alumina and trace of PU in the PU/ Al_2O_3 top layer (Fig. 2). The XRD curve detected from the surface of the PU/ Al_2O_3 -Al coating shows the major component as Al_2O_3 , apart from appearance of Al due to the thin thickness of the top layer. In this study, the overall coating thickness is $\sim 200\text{ }\mu\text{m}$, which can explain the non-appearance of XRD peaks for steel substrate. Even though the relative intensity of the diffraction peaks of the alumina in the coatings is much weaker than that of the untreated starting Al_2O_3 nanoparticles (Fig. 1a), no other peaks are observed for the coatings. This suggests unique advantages of better control over the chemistry of the nanostructured coatings offered by the suspension thermal spraying. The FTIR analyses suggest well-retained trace of PU in the PU/ Al_2O_3 top layer (Fig. 2b). The broad IR peak located at $400\text{--}1000\text{ cm}^{-1}$ is attributed to the Al–O bond (Fig. 2b). The peaks at 1567 cm^{-1} , 1731 cm^{-1} , and 1243 cm^{-1} are assigned to N–H, C=O and C–O–C groups, respectively, which are derived from PU [34,35]. PU possesses segmented structure on hydrogen bonds between N–H and C=O or ether oxygen atoms. The two peaks observed between 2957 cm^{-1} and 2874 cm^{-1} refer to the stretching vibrations of $-\text{CH}_2$ and $-\text{CH}_3$, respectively. The peak at 3445 cm^{-1} is attributed to both $-\text{OH}$ groups from the residual H_2O molecules and free N–H stretching vibration in PU. These results indicate the successful fabrication of the PU/ Al_2O_3 -Al coatings with perfectly retained structure of PU.

The as-sprayed Al coatings display relatively rough topographical morphology (Fig. 3a-1 and a-2). The thickness of the Al coating is $\sim 200\text{ }\mu\text{m}$ (Fig. 3a-3). Wettability assessment shows superhydrophilic characteristics of the arc-sprayed Al coatings with a contact angle of less than 5° . After the further deposition of the Al_2O_3 nanoparticles alone by suspension flame spraying on the Al coatings, the coating shows typical hybrid micro-/nano-structures on its surface with the thickness less than $2\text{ }\mu\text{m}$ (Fig. 3b). The coating also exhibits the feature of superhydrophilicity with a contact angle of less than 5° . This is likely due to the hydrophilic nature of the coated Al_2O_3 nanoparticles. In addition, it is realized that the matrix coating is not entirely covered by the Al_2O_3 nanoparticles. Full coverage is achieved by the 2.0 wt.% PU/ Al_2O_3 layer on the Al coating and the thickness of the PU/ Al_2O_3 layer is $\sim 35\text{ }\mu\text{m}$ (Fig. 3c). It is likely that the stability of the coating made from Al_2O_3 nanoparticles is improved after addition of PU which functions as an additional binder in the composite layer. Surprisingly, the 2.0 wt.% PU/ Al_2O_3 layer displays excellent hydrophobic property with the water contact angle of $\sim 151^\circ$. The water contact angle of PU film alone on silicon wafer is $\sim 94^\circ$, indicating that the superhydrophobicity of the PU/ Al_2O_3 layer is attributed to the synergies gained from the PU surface-functionalized Al_2O_3 nanoparticles. It is believed that apart from surface chemistry, surface roughness plays important roles in accomplishing the superhydrophobicity [36]. Generally, a superhydrophobic surface is known to be achieved by fulfilling both appropriate chemical composition and topographical structure. The surface profile in micro-/nano- scale

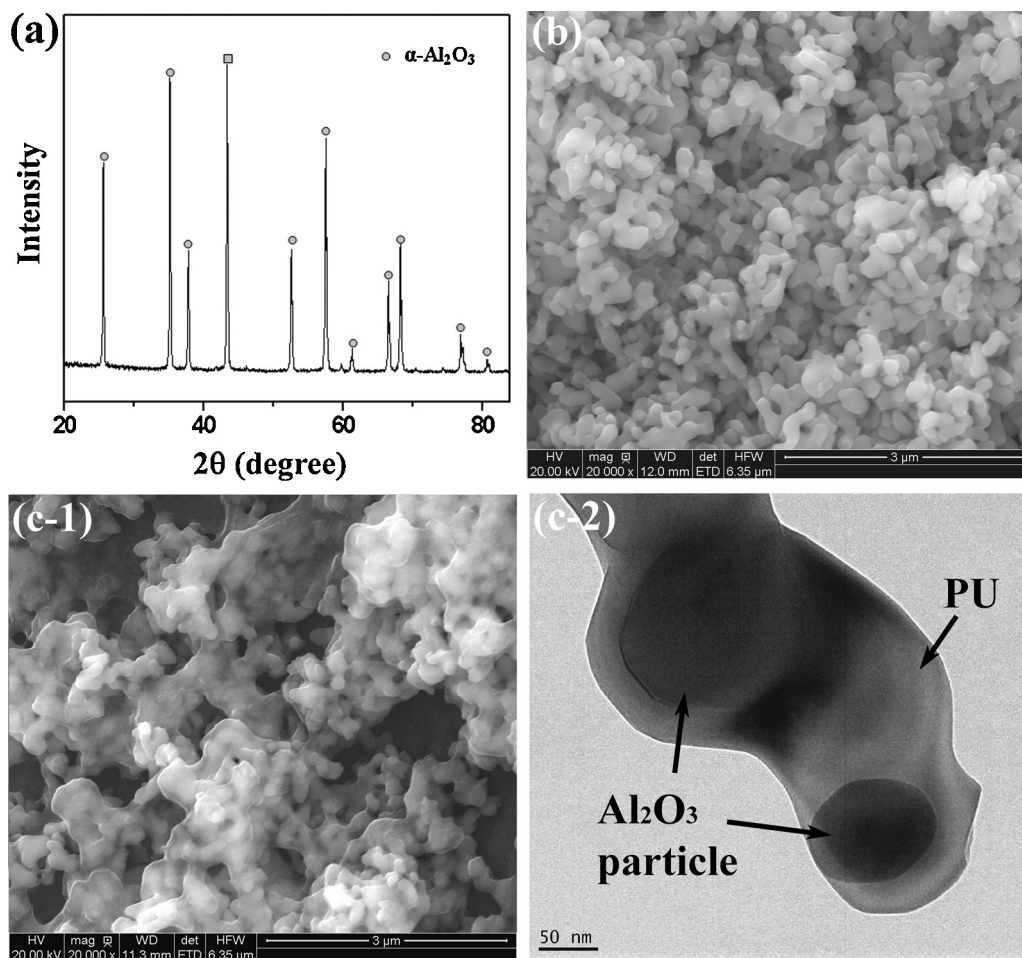


Fig. 1. Characterization of the starting particles and powder feedstock, (a) XRD curve of the starting Al₂O₃ particles, (b) FE-SEM image of the starting Al₂O₃ nanoparticles, and (c-1) FE-SEM and (c-2) TEM images of the PU treated Al₂O₃ nanoparticles.

and the surface energy in low level are essentially required for the materials like coatings to possess hydrophobic performance. Moreover, for fabricating superhydrophobic surface, expensive chemical reagents, e.g. perfluoroalkylsilane, thioalcohol, are usually used for attaining lower surface energy. However, some of the reagents especially fluorine-containing chemicals usually cause environmental problems [7]. The approach proposed in this paper provides an environment-friendly approach for fabricating superhydrophobic surfaces.

Thermal sprayed Al coating is one of the most efficient protective layers against corrosion for a variety of applications. For the marine

applications, apart from the need of dense microstructures, characteristics of the surfaces of the coatings in particular the surface wettability play important roles in deciding their anti-corrosion performances [5]. Systematical investigation shows that addition of PU altered the wettability of the surfaces of the coatings (Fig. 4). The coatings turn to be hydrophobic after addition of PU and increase in content of PU in the starting suspension brought about significantly increased water contact angles. The angle increases from ~62° for the top layer comprising 0.1 wt.%PU to ~151° for the layer comprising 2.0 wt.%PU. However, further increasing the PU concentration did not trigger further increase in water contact angle.

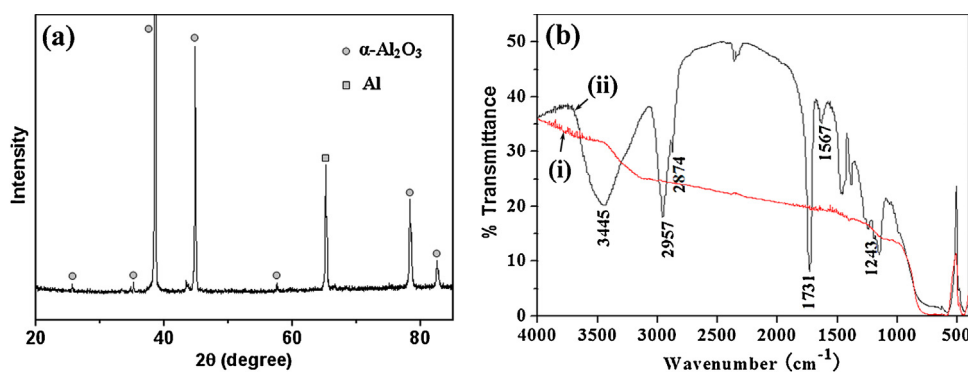


Fig. 2. (a) XRD curve of the 2.0PU/Al₂O₃/Al coating, and (b) FTIR spectra of the as-sprayed coatings (curve (i): the coating deposited using Al₂O₃ nanoparticle alone, and curve (ii): the coating deposited using the 2.0 PU/Al₂O₃ suspension).

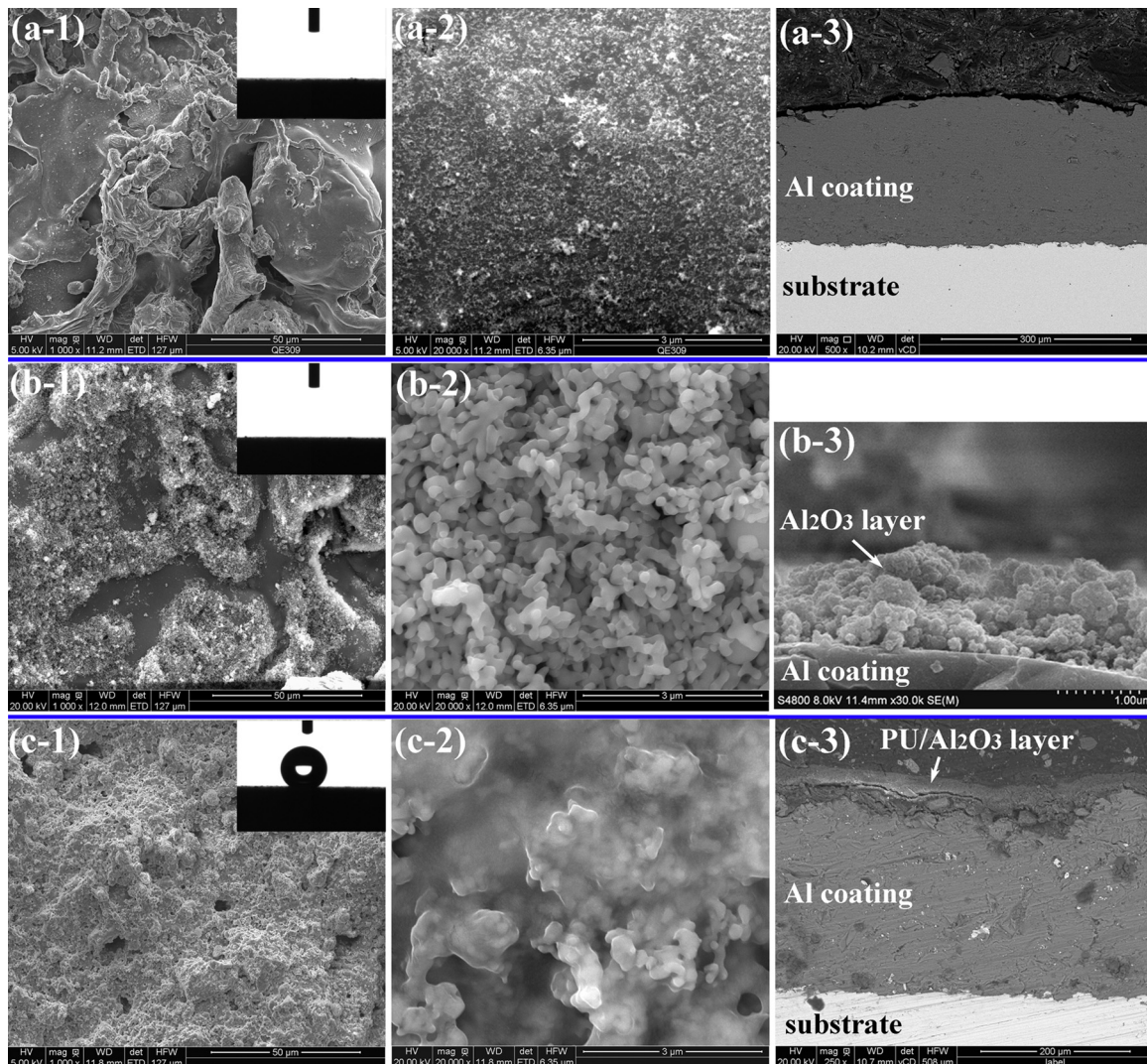


Fig. 3. FE-SEM images of (a) the as-sprayed Al coating, (b) the $\text{Al}_2\text{O}_3/\text{Al}$ coating, and (c) the 2.0 PU/ $\text{Al}_2\text{O}_3/\text{Al}$ coating. Insets are the images of water droplet placed on the coating samples. (–2 is enlarged view of selected area in –1, –3 is cross-sectional view of the coating).

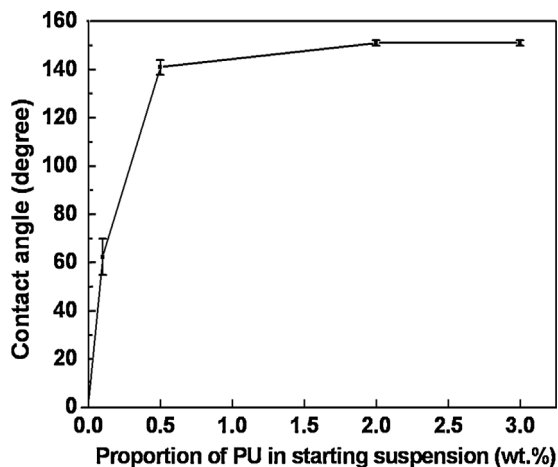


Fig. 4. Water contact angle of the PU/ $\text{Al}_2\text{O}_3/\text{Al}$ coatings versus the concentration of PU in the starting PU/ Al_2O_3 suspension.

Relatively low concentration of PU in the starting PU/ Al_2O_3 suspension (2.0 wt.% in this case) for the coating deposition already achieved superhydrophobicity, which would facilitate enhanced anti-corrosion performances of the coatings.

In practice, it is challenging for large-scale fabrication of anti-corrosion coatings with superhydrophobic surfaces. Extensive worldwide research efforts have been devoted to developing cost-effective methods for deposition of hydrophobic coatings. Thermal spray process offers the advantages of ease of on-site deposition of a wide variety of engineering materials. In this study, the superhydrophobic PU/ Al_2O_3 coatings were deposited on stainless steel with the dimension of 300 mm \times 300 mm \times 1.5 mm in length, width and thickness, respectively. Wettability assessment reveals that the water droplets standing on the coating surface exhibit spherical shape with a static contact angle of $\sim 151^\circ$ (Fig. 5), which agrees well with the previous findings for single droplet (Fig. 3c). Further testing shows that the as-deposited superhydrophobic surface is very slippery, showing a sliding angle of $\sim 6.5^\circ$ for water droplets (Fig. 5c). This might in turn assist the coatings to resist intimate contact of corrosive media.

The anti-corrosion performances of the superhydrophobic coatings were evaluated by potentiodynamic polarization testing conducted in 3.5 wt.% NaCl aqueous solution at room temperature. Fig. 6 shows the polarization curves of the Al coating and the

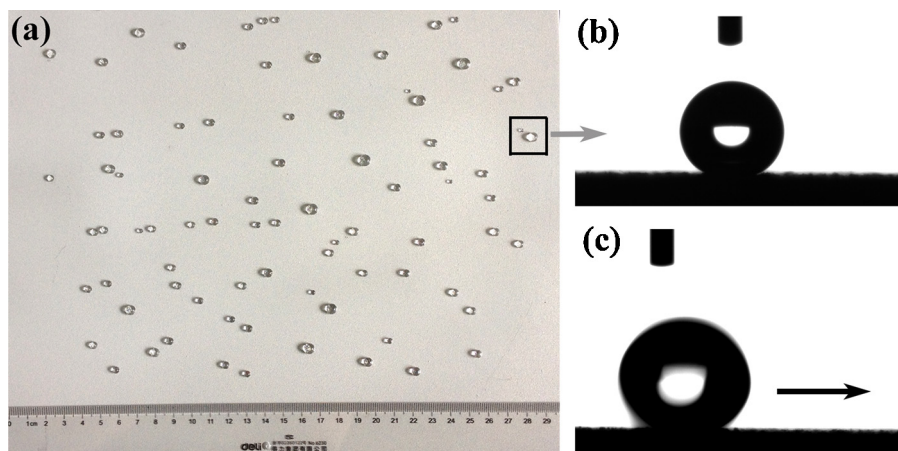


Fig. 5. Wettability testing results for the 2.0PU/Al₂O₃/Al coating showing superhydrophobic characteristics, (a) digital image of water droplets standing on the large-area superhydrophobic surface (300 mm × 300 mm), (b) static water contact angle measurement demonstrating a contact angle of ~151°, and (c) a sliding water droplet (10 μl) on the tilted coating surface (6.5°).

PU/Al₂O₃-Al coating. The corrosion potentials of the Al coating and the PU/Al₂O₃ coating are -1.357 V and -1.207 V, respectively. Corrosion potential is a measure of tendency of the sample to corrode, as higher corrosion potential indicates better corrosion resistance [37]. The positive shift in corrosion potential suggests the efficient protection by the superhydrophobic coating. Moreover, the corrosion current density of the Al coating, 2.215×10^{-3} A/cm², is much higher than that of the superhydrophobic coatings, 1.873×10^{-4} A/cm². It is established that a lower corrosion current density or a higher corrosion potential denotes lower corrosion rate and better corrosion resistance [38]. It is worthwhile to notice that the corrosion current density was reduced by almost one order after the construction of a superhydrophobic layer on the Al coating. Such low current density indicates significantly enhanced corrosion resistance. This is consistent with the findings reported previously that hydrophobic surface can provide corrosion protection for substrates [4,20,21,39]. Obviously the water repellent feature of the superhydrophobic surface provides the coatings with the capability of preventing the corrosion attack in the NaCl aqueous solution [9]. Corrosion-resistant Al coatings usually suffer from their relatively porous structure during long-term service. The microstructure characterization of the coatings already suggested densified topographical microstructure by the deposition of nano-Al₂O₃ (Fig. 3b). Furthermore, addition of PU further improved the structure of the

coatings at their surfaces (Fig. 3c), which is attributed to the fact that PU most likely functions as additional binder in the composite layer. The layer presumably inhibits effectively migration and penetration of chloride ions (corrosive ions) into the Al coating, consequently enhancing the anti-corrosion performances of the coatings. The novel cost-effective superhydrophobic coatings could be potentially used for a variety of anti-corrosion applications.

4. Conclusions

Superhydrophobic PU/Al₂O₃ thin layer was constructed by suspension flame spraying on arc-sprayed aluminum coatings. The wettability of the coating surfaces can be tailored by adjusting the concentration of PU in the starting PU/nano-Al₂O₃ suspension. The superhydrophobic surface with a water contact angle of ~151° and the sliding angle of ~6.5° was obtained for the layer containing 2.0 wt.%PU. The dense superhydrophobic PU/nano-Al₂O₃ coating significantly enhanced the anti-corrosion performances of the Al coatings through resisting effectively diffusion of corrosive agents into the coatings. The present study provides a simple and environment-friendly method for large-scale fabrication of superhydrophobic corrosion-resistant coatings for marine applications.

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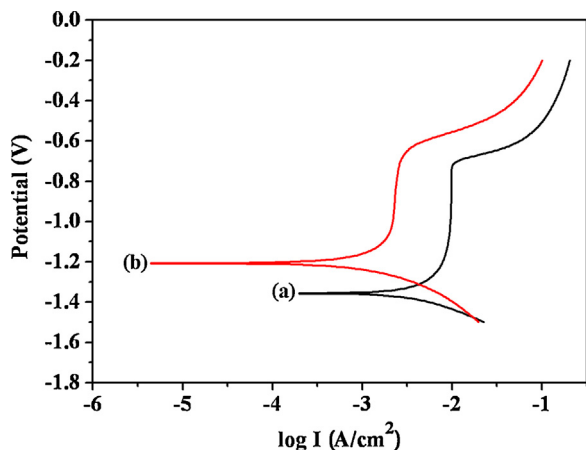


Fig. 6. Potentiodynamic polarization curves of (a) the superhydrophilic Al coating and (b) the superhydrophobic PU/Al₂O₃/Al coating measured in 3.5 wt.% NaCl aqueous solution.

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